Disentangling the role of linear transition dipole in band-edge emission from single CdSe/ZnS quantum dots: Combined linear anisotropy and defocused emission pattern imaging

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Combined linear anisotropy and defocused wide-field fluorescence imaging of individual CdSe/ZnS quantum dots reveal an unambiguous contribution of a linear transition dipole polarized along the hexagonal (c-) symmetry axis of the nanocrystal which grows with increasing tilt angle of the c-axis with respect to the surface normal. These results offer some insights into quantum dot luminescence polarization dynamics, and provide a basis for unambiguously assigning the two Euler angles describing the c-axis orientation from defocused emission patterns for multidipole systems. © 2010 American Institute of Physics. [doi:10.1063/1.3488669]

Defocused wide-field fluorescence imaging has provided a powerful tool for investigating orientational dynamics of linear dipole systems.\textsuperscript{1,2} Commonly implemented by a controlled (z-) translation of the sample a small distance from the focal plane (typically 500–1000 nm), the induced phase aberration presents a type of k-space image at the detector that is uniquely defined for the Euler angles Θ and Φ of the transition dipole relative to the surface normal.\textsuperscript{3} Recently, this technique has been applied to quantum dots\textsuperscript{4-8} and chiral systems\textsuperscript{9,10} that possess multiple dipole components. Such systems have been shown to generate qualitatively different defocused images compared to perfect linear dipole systems. Extracting accurate orientation information from the defocused images of multidipole systems is difficult due to the large number of adjustable parameters (i.e., dipole strength, relative orientation angles, phase, etc.), as well as the strong dependence on electrodynamic source models that have not been confirmed independently.

In this paper, we explore the wide-field defocused fluorescence imaging of single CdSe/ZnS quantum dots combined with in situ linear polarization anisotropy measurements of the band edge emission. These measurements provide a direct test of the two-dimensional degenerate dipole (2D-DD) model for colloidal semiconductor nanocrystals and yield quantitative information on the contribution of a third dipole component polarized along the c-axis of the nanocrystal. These results offer insights into quantum dot luminescence polarization dynamics,\textsuperscript{11,17} and provide a basis for unambiguously assigning orientation Euler angles from defocused emission patterns (DEPs) for multidipole systems.

The band-edge luminescence in CdSe QDs can be associated primarily with two different electron-hole fine structure states that are driven by right- and left-circularly polarized radiation, respectively; equal contribution of the two transitions gives rise to the 2D-DD picture of QD emission.\textsuperscript{11,14} The projection of this 2D disk onto the detector x-y plane gives rise to a polarization anisotropy with contrast parameter, M, ranging from 0 to 1, depending on the tilt angle of c-axis with respect to the surface normal. However, as described by Efros\textsuperscript{15} and others,\textsuperscript{16} a third linear transition dipole polarized along the c-axis of the nanocrystal, usually referred to as the “dark-axis,” affects both DEP and linear anisotropy.\textsuperscript{15,16} Transitions polarized along the c-axis of the nanocrystal are nominally forbidden but mixing of electron/hole states via exchange interactions or shape anisotropy can relax this selection rule.\textsuperscript{16} In defocused imaging, the contribution of this third dipole component to DEPs is subtle. Recently, Schuster and co-workers reported an apparent ellipticity in QD luminescence inferred by distortion in measured DEPs,\textsuperscript{4} and similar effects have been observed in the DEPs of chiral fluorophores.\textsuperscript{9} Likewise, Bohmer and Enderlein have developed a parameterized model to account for ellipticity and third dipole components. However, determining a unique set of fitting parameters adds considerably to analysis time and is very sensitive to the signal to noise ratio in the image.

Our experiments reported here were designed to disentangle the contribution of different polarization components in the QD luminescence by combining measurements of the DEP and linear anisotropy traces.\textsuperscript{14,17} For excitation near the band edge of the QD sample, we find that, for small tilt angles (~50°) modulation depth of the linear dichroism data is in close agreement with predictions from a 2D disk model. For larger tilt angles (>60°), however, we find a significant deviation between observed modulation depths and those expected from a 2D disk model. We show that inclusion of a third dipole with a tilt-angle dependent contribution ranging from 0.00 to 0.42 (relative to the magnitude of the X dipole component) can bring the two measurements into agreement, thus providing a quantitative measure of the contribution of the transition dipole moment along the c-axis of the nanocrystal.

Figure 1 shows a schematic of the experimental setup and geometry of a quantum dot. The internal QD coordinate frame was labeled with unit vectors $\mathbf{X}$, $\mathbf{Y}$, and $\mathbf{c}$, where the c-axis orientation was defined by the Euler angles $\Theta$ and $\Phi$. The $\mathbf{x}$ and $\mathbf{y}$ coordinates of the charge-coupled device (CCD) camera used to make the DEP measurements are registered with a linear polarization analyzer (i.e., polarization along

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Individual CdSe/ZnS quantum dots (Evidot, 4.2 nm core) were excited in an epi-illumination geometry using either 514.5 or 457 nm left-circular polarized radiation from a cw argon ion laser. A 1.4 numerical aperture, 100x oil immersion objective was used to collect the fluorescence viewed through a 560 long pass dichroic filter and a 605/50 band pass filter removed excess excitation light. DEPs were obtained by translating the sample off the z-axis by 800–900 nm using a servo-controlled stage and provide an estimate of c-axis orientation. Linear anisotropy traces were obtained by diverting the QD fluorescence to the microscope side-port through a Notch filter (OD ≥ 6) centered at 514.5 or 457 nm, where the fluorescence intensity was measured through a rotating linear analyzer mounted on a servo-controlled rotation stage (Newport 8401, 0.6 rad/s), and detected on a separate CCD camera (Princeton Instruments Photomax). The modulation depth (M=I_{max}−I_{min}/I_{max}+I_{min}) and the phase of the linear anisotropy were extracted by fitting the intensity data to Eq. (1)

$$I(\theta) = I_{\text{max}}[1 - M \cos^2(\theta - \delta)],$$

where $\theta$ is the angle of the transmission axis of the linear analyzer, $M$ is the contrast parameter (M=I_{max}−I_{min}/I_{max}+I_{min}), and $\delta$ is the phase-offset related to the Euler angle $\Phi$ by $\delta = \Phi \pm \pi/2$.

The DEPs were analyzed using a modified version of linear dipole simulator based on the model of Hellen and Axelrod, using a 2D-DD as the electrolytic source, modeled as an incoherent sum of X and Y dipoles rotated in the laboratory frame by Euler angles $\Theta$ and $\Phi$. The experimental defocused images were matched to simulations by searching a library of simulated images on a 5° grid in $\Theta$ and $\Phi$, using a pixel-by-pixel $\chi^2$ criterion, yielding Euler angle uncertainties of ±5°. Similar models have been discussed by Enderlein, Schuster, and Hermier.

We estimated the c-axis orientation from analysis of the DEP, then compared the modulation depth and phase anticipated from a 2D disk model experimental, with the values obtained directly from the linear dichroism data. Projection of the 2D polarization disk into the detector x-y plane should give a modulation depth proportional to $\sin(\Theta)$, and a phase, $\delta=\Phi \pm \pi/2$. In the limit where $\epsilon$ is perpendicular to the optic axis, the 2D disk appears to the detector as a one-dimensional dipole, with modulation depth approaching unity.
DD) to be 75°. The magnitude of this Z dipole was determined by varying the magnitude to match the experimentally measured modulation depth, in this case a projected dipole magnitude of 0.42 (relative to the magnitude of the X-axis dipole). Linear dichroism data provides the magnitude of the Z-dipole for simulated DEPs using 2D-DD and 2D-DD+Z dipole. These models are very similar, although the $\chi^2$ parameter associated with the fit to the experimental DEP decreases by significantly on inclusion of the Z-dipole. We hypothesized that the amplitude of the Z-dipole might be dependent on phonon excitation, thus possibly showing an increase in amplitude with higher energy excitation above the band gap. Using 457 nm excitation similar Z-dipole amplitude dependence was observed with tilt angle, however, the magnitudes appeared indistinguishable.

It is interesting to speculate on the origin of the phase differences between the experimentally determined phase of the linear anisotropy and that predicted by the 2D disk projection model. In the experiment, the DEPs are acquired with a moderately long single exposure (2 s). Following, the linear anisotropy data is accumulated for multiple dots over total integration times spanning several minutes. While much of the polarization data is selected from quantum dots that show minimal blinking, there is direct evidence in many of the traces of a phase-jitter correlated with fluorescence intermittency. Since the phase parameter in the simulation is assigned from the DEP, it is conceivable that stochastic polarization rotations during blinking alter the phase of the measured linear anisotropy data. In addition, recent work by Pelton and co-workers has shown interesting orientation-dependent differential coupling of transition dipole components of QDs near a conducting interface.

We have shown how combined defocused imaging and linear polarization anisotropy measurements on individual quantum dots provide a quantitative test of the 2D-DD model of quantum dot emission, and the role of nominally forbidden transitions polarized along the c-axis in defining polarization characteristics from single quantum dots. In many of the dots sampled the 2D degenerate disk model provides a highly accurate description of c-axis orientation and the related polarization characteristics in both modulation depth and phase. However, an additional dipole component is apparent that reduces polarization contrast. The contribution of this nominally forbidden polarization component appears to be independent of excitation wavelength, yet increases with increasing tilt angle of the c-axis with respect to the surface normal. While differences in experimentally determined modulation depth (from linear anisotropy) and expectations from 2D-DD can be understood by adding a weak Z-dipole, there are interesting and significant phase differences that are currently not understood. We speculate that these could arise from “polarization rotation” effects associated with charge trapping during blinking on/off cycles; we observe the best phase agreement for QDs with minimal blinking. Disentangling these different transition moment contributions to the DEPs and linear anisotropy will ultimately be helpful in understanding more complicated transition dipole structure in chiral nanomaterials.

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